of 1,4-naphthoquinone some epoxide was, indeed, produced, but in very low yield and only after reaction times of the order of several days at room temperature. Most of the starting material was recovered unchanged. No detectable amount of epoxide was formed in the reaction of the 2-methyl-1,4-naphthoquinone with hypochlorous acid. It appears that the formation of epoxide from naphthoquinone in contact with aqueous hypochlorous acid was due to the reaction with the hypochlorite ion, which is present in very low concentration.

Experimental[8]

Epoxidation of Benzalacetophenone.—To a solution of 1.0 g. (0.048 mole) of benzalacetophenone in 7.5 ml. of pyridine was added 11 ml. of fresh 5.25% sodium hypochlorite solution (Clorox). The yellow color of the solution faded almost immediately and heat was evolved.[9] When the mixture became colorless, or nearly so, 25 ml. of water was added, causing the precipitation of the white crystals of the epoxide. The product was filtered, washed thoroughly with water and then recrystallized from ethanol. There was obtained 1.0 g. (94%) of the epoxide, m.p. 89–90°. The identity of the compound was verified by a mixed melting point determination with an authentic sample of 1,3-diphenyl-2,3-epoxy-1-propanone, prepared by the method of Weitz and Scheffer.[1] The infrared spectra of the prepared compound and the authentic sample were identical.

trans-Dibenzoylethylene oxide was prepared in the manner described above from *trans*-dibenzoylethylene. A 93% yield of the epoxide, m.p. 131.5–132.0°, was obtained. The identity was verified by a mixed melting point determination and comparison of infrared spectra with an authentic sample.

Epoxidation of 1,4-Naphthoquinone.—Ten milliliters of 5.25% sodium hypochlorite was added to a solution of 1.0 g. of 1,4-naphthoquinone in 20 ml. of dioxane. Heat was evolved and the mixture was cooled by an external water bath. After 2 min., the mixture was pale yellow and remained the same color for an additional minute. Thirty-five milliliters of water was added and the light yellow precipitate was recovered by filtration. After washing thoroughly with water, the crude product was recrystallized from ethanol. A yield of 0.8 g. (71.5%) was realized. The melting point of the product and that of a mixture of the product with 2,3-epoxy-2,3-dihydro-1,4-naphthoquinone was 134–136°.

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(8) All melting points are uncorrected.

(9) It would be advisable to provide external cooling if the reaction is run on a larger scale.

The Stereochemical Configuration of 5-Hydroxylysine and Synthesis of (+)-1,5-Diamino-2-hydroxypentane (Hydroxycadaverine)[1]

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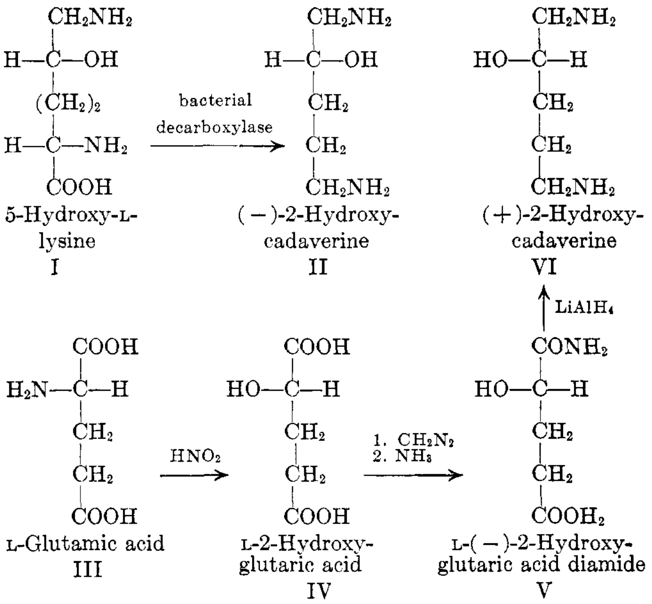
5-Hydroxylysine remains as the last of the protein-bound amino acids for which the stereochemical configuration has not been definitely established by chemical means.



Witkop has applied Hudson's lactone rule to *N*-acylated derivatives of hydroxyamino acids. From the results obtained with natural 5-hydroxylysine[2] he concluded that this amino acid should have the *erythro* configuration.

We have recently studied the decarboxylation of 5-hydroxylysine by bacterial L-lysine decarboxylase.[3] The natural isomer I gave the levorotatory dihydrochloride of 1,5-diamino-2-hydroxypentane [(−)-2-hydroxycadaverine] II, ($[\alpha]^{25}_{589}$ −14.8°]) from which a levorotatory dibenzoate was prepared.

This communication describes the synthesis of the dextro isomer of 2-hydroxycadaverine VI by a route which establishes its absolute configuration and consequently that of the second asymmetric center in 5-hydroxy-L-lysine. The steric correlation is shown in the Fischer projection formulas of the compounds involved. Deamination of L-glutamic acid III is known to proceed with retention of configuration[4] to yield L-2-hydroxyglutaric acid IV. This hydroxy acid was converted to the levorotatory diamine V which on reduction with lithium aluminum hydride in boiling diglyme[5] gave the dextrorotatory diamine dihydrochloride VI ($[\alpha]^{28}_{589}$ +11.1°).

On benzoylation in sodium hydroxide a dextrorotatory dibenzoate ($[\alpha]^{21}_{589}$ +23.6°) was obtained which was identical in melting point and infrared spectrum with the levo-compound, ($[\alpha]^{25}_{589}$ −21.6°), obtained after benzoylation of the amine II formed in decarboxylation of natural 5-hydroxy-L-lysine. These results confirm the *erythro* configuration deduced by Witkop[2] from rotational measurements.

Experimental

L-2-Hydroxyglutaric Acid.—L-Glutamic acid (Merck Co.) was deaminated with nitrous acid[6] and the hydroxyglutaric acid isolated as a crude barium salt.

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(1) Supported by a grant from Riksföreningen mot Reumatism.

(2) B. Witkop, *Experientia*, **XII**, 372 (1956).

(3) S. Lindstedt and G. Lindstedt, *Arkiv Kemi*, **19**, 447 (1962).

(4) C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, New York, N. Y., 1953.

(5) Diglyme = dimethyl ether of diethylene glycol.

(6) E. Fischer and A Moreschi, *Ber. Deut. Chem. Ges.*, **45**, 2447 (1912).

2-Hydroxyglutaric Acid Diamide.—A solution of 7 g. of the barium salt of L-2-hydroxyglutaric acid in 40 ml. of water was passed through a short column of the cation exchanger Dowex-50 × 4 (50–100 mesh, H$^+$-form). The column was washed with water and the combined effluents evaporated to dryness *in vacuo* at 30°. The residual oil, 3.5 g., was kept in the desiccator overnight, dissolved in 20 ml. of ice-cold methanol and esterified with diazomethane to yield 4.1 g. of crude dimethyl 2-hydroxyglutarate. This material, 3.5 g., was dissolved in 20 ml. of dry methanol and the solution saturated with ammonia at 0°. After keeping for 24 hr. at room temperature 2.7 g. of the diamide was filtered off, m.p. 181–182° (lit.,[7] 182°) $[\alpha]^{22}_{589}$ −33°, (l 2; c 1.48 in water).

Anal. Calcd. for $C_5H_{10}O_3N_2$ (146.15): C, 41.09; H, 6.90; N, 19.17. Found: C, 41.03; H, 6.79; N, 18.79.

(+)-1,5-Diamino-2-hydroxypentane Dihydrochloride.—The L-2-hydroxyglutaric acid diamide, 0.5 g., was placed in a small filter paper thimble in the neck of a flask fitted with a reflux condenser. The flask contained a suspension of 1.0 g. of lithium aluminum hydride in 50 ml. of refluxing diglyme.[8] After 20 hr. the amide had been extracted into the boiling solution. After cooling excess lithium aluminum hydride was decomposed with 3 ml. of water followed by 3 ml. of 1 *N* sodium hydroxide. The precipitate was filtered off and washed with hot ethanol. After adjusting to pH 3 the solution was evaporated and the residue put onto a column of Dowex-50 × 4 (200–400 mesh; 54 × 1.2 cm. in 1 *N* hydrochloric acid). The column was eluted with 1 *N* hydrochloric acid (200 ml.) followed by 3 *N* hydrochloric acid which eluted the hydroxyamine after further 70–80 ml. effluent. The amine hydrochloride crystallized on evaporation of the hydrochloric acid *in vacuo* and was recrystallized twice from ethanol to give 0.08 g. of m.p. 166–167°, $[\alpha]^{28}_{589}$ +11.1°, (l 1; c 2 in water).

Anal. Calcd. for $C_5H_{16}ON_2Cl_2$ (191.1): C, 31.42; H, 8.44; N, 14.66. Found: C, 31.52; H, 8.47; N, 14.11.

(+)-1,5-Dibenzamido-2-hydroxypentane.—(+)-1,5-Diamino-2-hydroxypentane dihydrochloride, 0.09 g., were dissolved in 5 ml. of 1 *N* sodium hydroxide and 0.4 ml. of benzoyl chloride added in portions with stirring. After standing overnight in the refrigerator 0.08 g. of crystals were filtered off and recrystallized from ethyl acetate, m.p. 130–32°, $[\alpha]^{21}_{589}$ +23.6° (l 1; c 0.84 in pyridine).

Anal. Calcd. for $C_{12}H_{22}O_3N_2$ (326.4): C, 69.92; H, 6.77; N, 8.59. Found: C, 70.08; H, 6.96; N, 8.61.

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(7) C. Ravenna and R. Nuccorini, *Gazz. chim. ital.*, **58**, 861 (1928).

(8) Dried over calcium hydride and redistilled from lithium aluminum hydride.

The Chemistry of Ylids. VIII. Synthesis of Nitrones *via* Sulfur Ylids[1]

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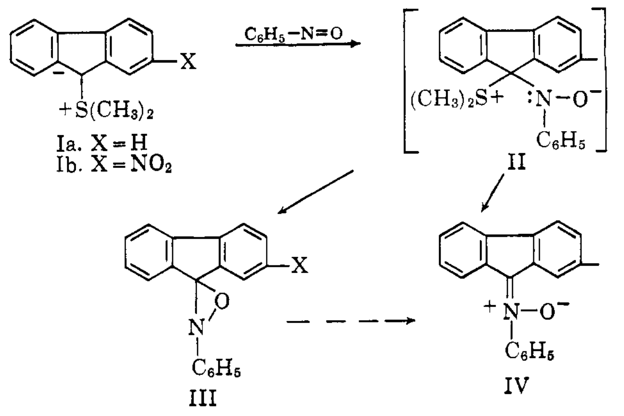
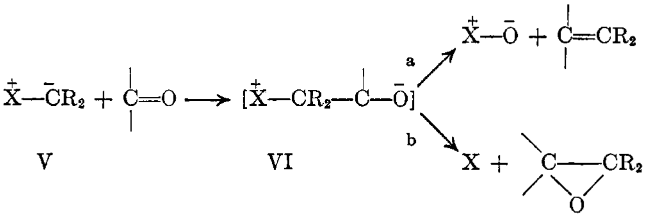
In our original report on the preparation and reactions of sulfur ylids[2] we noted briefly that 9-dimethylsulfoniumfluorenylide (Ia) reacted with nitrosobenzene to form what appeared to be N-phenylfluorenone ketoxime (IVa) rather than the expected oxazirane (IIIa). We wish to report further studies on this reaction.

It has been well established[3] that phosphorus- and arsenic-containing ylids (V. X = PR'$_3$, AsR'$_3$) react with carbonyl compounds by initial attack of the ylid carbanion on the carbonyl carbon to form an intermediate betaine (VI). The reaction goes to completion *via* a four-membered transition state resulting in the ultimate formation of an olefin and the appropriate phosphine oxide or arsine oxide (path a). It has been shown[4] that these same ylids will react with nitrosobenzene in an analogous fashion to form the expected N-phenylimines. For example, triphenylphosphoniumfluorenylide and nitrosobenzene afforded fluorenone anil in 84% yield.[4a]





Johnson and LaCount[2] have recently shown that sulfur ylids (V. X = SR'$_2$) also react with carbonyl compounds by attack of the ylid carbanion on the carbonyl carbon to form a similar betaine intermediate. However, the oxyanion portion of this betaine (VI. X = SR'$_2$) displaced the sulfide group forming an epoxide as the major product (path b). By analogy it was expected that sulfur ylids would react with nitrosobenzene to form oxaziranes (III), thereby providing another synthetic route to these unique compounds. Oxaziranes have been intensely studied since their original synthesis by Emmons.[5]

An exothermic reaction took place upon mixing the ylid (Ia) and nitrosobenzene, ultimately affording a quantitative yield of the *nitrone* (IVa). Microanalytical data and hydrolysis of the product to fluorenone were both consistent with either structure IIIa or IVa. That the product was, in fact, the nitrone (IVa) and not isomeric oxazirane (IIIa) was demonstrated by infrared absorption at 6.06 μ (C=N), 6.51 and 7.48 μ (N=O) and by the ultraviolet spectrum which showed the long wave length absorption (351 mμ) expected of a fluorenylidene system and not the simple fluorenyl spectrum expected for IIIa. The substance was also shown to react in a 1,3-addition reaction with diethyl fumarate to form an isoxazolidine.[6]

The generality of this reaction was demonstrated using 9-dimethylsulfonium-2-nitrofluorenylide (Ib) and dimethylsulfonium(diphenyl)methylide, both of which afforded the corresponding nitrones in good yield when

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(1) (a) We gratefully acknowledge the financial support of the National Science Foundation through Grant No. G-17345; (b) for the previous paper in this series see A. W. Johnson and V. J. Hruby, *J. Am. Chem. Soc.*, **84**, 3586 (1962).

(2) A. W. Johnson and R. B. LaCount, paper VI, *ibid.*, **83**, 417 (1961).

(3) G. Wittig, H. D. Weigmann, and M. Schlosser, *Chem. Ber.*, **94**, 676 (1961); A. W. Johnson and R. B. LaCount, *Tetrahedron*, **9**, 130 (1960).

(4) (a) A. W. Johnson, unpublished observations; (b) A. Schonberg and K. H. Brosowski, *Chem. Ber.*, **92**, 2602 (1959).

(5) W. D. Emmons, *J. Am. Chem. Soc.*, **79**, 5739 (1957).

(6) G. R. Delpierre and M. Lamchen, *Proc. Chem. Soc.*, 386 (1960).